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## Preparation of xylylenediamine (XDA)

The present invention relates to a process for preparing xylylenediamine, comprising the steps of

5 ammonoxidizing xylene to phthalonitrile by contacting the vaporous product of the ammonoxidation stage directly with a liquid organic solvent (quench) and hydrogenating the phthalonitrile in the resulting quench solution or suspension.

Xylylenediamine (bis(aminomethyl)benzene) is a useful starting material, for example

10 for the synthesis of polyamides, epoxy hardeners or as an intermediate for preparing isocyanates.

The term "xylylenediamine" (XDA) includes the three isomers ortho-xylylenediamine, meta-xylylenediamine (MXDA) and para-xylylenediamine.

15 The term "phthalonitrile" (PN) includes the three isomers, 1,2-dicyanobenzene = o-phthalonitrile, 1,3-dicyanobenzene = isophthalonitrile = IPN and 1,4-dicyanobenzene = terephthalonitrile.

20 The two-stage synthesis of xylylenediamine by ammonoxidizing xylene and subsequently hydrogenating the resulting phthalonitrile is known.

25 EP-A2-1 113 001 (Mitsubishi Gas Chem. Comp.) describes a process for preparing nitrile compounds by ammonoxidizing corresponding carbocyclic or heterocyclic compounds, in which excess ammonia from the reaction product is recycled. Also described is the direct contacting of the vaporous product of the ammonoxidation stage with a liquid organic solvent which is in particular aliphatic or aromatic hydrocarbons (paragraphs [0045] and [0046]).

30 EP-A2-1 193 247 and EP-A1-1 279 661 (both Mitsubishi Gas Chem. Comp.) relate to a process for purifying isophthalonitrile (IPN) and to a process for preparing pure XDA respectively, in which the phthalonitrile is synthesized by ammonoxidizing xylene, and the vaporous product of the ammonoxidation stage is contacted directly with a liquid organic solvent (quench). The organic solvent is selected from alkylbenzenes, heterocyclic compounds, aromatic nitriles and heterocyclic nitriles, and has a boiling point which is below that of phthalonitrile (EP-A2-1 193 247: column 4, paragraph [0018] and [0019]; EP-A1-1 279 661: columns 4-5, paragraph [0023] and [0024]).

40 EP-A2-1 193 244 (Mitsubishi Gas Chem. Comp.) describes a process for preparing XDA by hydrogenating phthalonitrile which is synthesized in a preceding stage by ammonoxidizing xylene, in which the vaporous product of the ammonoxidation stage is contacted directly with a liquid organic solvent (quench) and the resulting quench solution or suspension is fed to the hydrogenation.

Preferred organic solvents are C<sub>6</sub>-C<sub>12</sub> aromatic hydrocarbons such as xylene and pseudocumene (column 6, paragraph [0027] and [0028]).

5 DE-A-21 64 169 describes, on page 6, last paragraph, the hydrogenation of IPN to meta-XDA in the presence of an Ni and/or Co catalyst in ammonia as a solvent.

Five parallel BASF patent applications each having the same application date each relate to processes for preparing XDA.

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It is an object of the present invention to provide an improved, economically viable process for preparing highly pure xylylenediamine, in particular meta-xylylenediamine, with high yield and space-time yield (STY), which, at comparable throughputs to prior art processes (for example EP-A2-1 193 244), enables smaller apparatus and

15 machines as a consequence of reduced streams, in particular solvent streams, including recycle streams.

We have found that this object is achieved by a process for preparing xylylenediamine, comprising the steps of ammoxidizing xylene to phthalonitrile by contacting the

20 vaporous product of the ammoxidation stage directly with a liquid organic solvent (quench), and

hydrogenating the phthalonitrile in the resulting quench solution or suspension, wherein the organic solvent is N-methyl-2-pyrrolidone (NMP).

25 The process according to the invention preferably finds use for preparing meta-xylylenediamine (MXDA) by hydrogenating isophthalonitrile (IPN) which is synthesized in a preceding stage by ammoxidizing meta-xylene.

The process according to the invention can be performed as follows:

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Ammoxidation stage:

The ammoxidation of xylene (o-, m- or p-xylene) to the corresponding phthalonitrile (ortho-xylene → o-phthalonitrile; meta-xylene → isophthalonitrile; para-xylene →

35 terephthalonitrile) is generally carried out by processes known to those skilled in the art.

The ammoxidation of methyl aromatics is preferably carried out over a multioxide catalyst with ammonia and an oxygenous gas (oxygen or air or both) in a fluidized bed reactor or a tube (bundle) reactor.

40 The reaction temperature is generally from 300 to 500°C, preferably from 330 to

480°C.

5 The catalyst preferably contains V, Sb and/or Cr and is more preferably composed of [V, Sb and alkali metals] or [V, Cr, Mo and B], in each case as an unsupported catalyst or on an inert support.

Preferred inert supports are SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or a mixture of both, or steatite.

10 Such a procedure is described, for example, in the BASF patent applications EP-A-767 165 and EP-A-699 476, which are explicitly incorporated herein by way of reference.

15 The BASF patent applications EP-A-222 249, DE-A-35 40 517 and DE-A-37 00 710 also disclose suitable ammonoxidation catalysts.

15 The ammonoxidation may also be carried out in accordance with the processes described in the applications cited at the outset, EP-A2-1 113 001, EP-A2-1 193 247, EP-A1-1 279 661 and EP-A2-1 193 244.

20 Quench:

25 The vapor produced in the ammonoxidation, comprising the product of value, phthalonitrile, is contacted directly with the liquid organic solvent N-methyl-2-pyrrolidone (NMP) (quench with NMP as a quench liquid, quenching agent).

25 The NMP used for the quench may already contain dissolved or suspended phthalonitrile (preferably that isomer which corresponds to the synthesized PN).

30 The sudden temperature reduction when contacting the vaporous phthalonitrile with the liquid solvent NMP (quench) reduces the formation of undesired secondary and decomposition products which lead to a reduction in the quality of the phthalonitrile and finally of the XDA.

35 The vaporous phthalonitrile is absorbed by the quench directly into the liquid NMP solvent, resulting in a solution and/or a suspension which may be further processed directly.

40 In general, technical-grade NMP having a purity > 99% by weight, in particular > 99.5% by weight is used as the fresh feed.

40 Preference is given to using NMP recovered from the process as the quench liquid. The purity here of the quench liquid may also be ≤ 99% by weight, for example 90-98%

by weight, especially when the impurities are substances which are not foreign to the process (i.e., *inter alia*, water, ammonia, benzonitrile, tolunitrile, xylene, o-, m- or p-methylbenzylamine, benzylamine, xylylenediamine).

5 The amount of the NMP solvent used is generally such that solutions/suspensions are obtained which have a phthalonitrile content of from 15 to 75% by weight, preferably from 25 to 60% by weight.

10 The vaporous effluent of the ammonoxidation, comprising the phthalonitrile (PN), is introduced into the NMP in a quench apparatus, for example preferably in a falling-film condenser (thin-film, trickle-film or falling-stream condenser), in a jet apparatus or in a column. In this apparatus, the vaporous phthalonitrile may be conducted in cocurrent or in countercurrent with the liquid solvent. In the case of cocurrent flow, the vaporous phthalonitrile is introduced into the quench apparatus from above. It is advantageous to 15 feed the liquid solvent tangentially at the top of the falling-film condenser or to feed the liquid solvent through one or more nozzles, in order to achieve complete wetting of the interior wall of the quench apparatus.

20 In the case of a quench column, the gas from the ammonoxidation is introduced at the bottom of the column and the solvent is fed at the top. To increase the surface area available for condensation, the quench apparatus may be equipped with internals such as trays, structured packings or random packings.

25 The NMP for the quench may be used in single pass or as circulation medium.

Advantageously, a portion of the quench solution or suspension is recycled.

30 A heat transferor installed in the circuit is used to cool the quench solution or suspension.

35 The temperature of the circulation medium and the circuit flow rate are set and adjusted with respect to each other in such a way that the desired temperature in the quench exit is achieved. The smaller the flow rate of the circulation medium, the lower the temperature selected of the circulation medium and vice versa, although solubilities and melting points, and also the hydraulic stress limits of the quench apparatus, have to be taken into account.

40 The flow rate of the freshly fed NMP is dependent upon the quench temperature since, as the temperature increases, more solvent is present in the vaporous quench effluent.

It is set in such a way that the desired concentration of the PN solution or suspension is obtained. Since the solubility of PN in NMP rises with increasing temperature, a higher

PN concentration in the NMP can be conveyed with increasing quench exit temperature.

5 The circulation medium is fed in together with the fresh solvent or separately, at a suitable point in the quench apparatus.

In the case of a quench column operated in countercurrent, the fresh NMP is fed at the top and the circulation medium further down, in about the middle of the column.

10 In general, heating of the NMP and/or of the circulation medium used sets the temperature of liquid quench effluent to from 40 to 180°C, preferably from 50 to 120°C, in particular from 80 to 120°C.

15 In the range from 1 to 100 mbar, the boiling point of phthalonitrile is approx. 60 kelvin above the boiling point of NMP.

The absolute pressure in the course of quenching is generally from 0.5 to 1.5 bar. Preference is given to operating at slightly elevated pressure.

20 Xylene, water, NH<sub>3</sub>, CO<sub>2</sub>, N<sub>2</sub>, etc., which are generally present in the vaporous effluent of the ammonoxidation are only partly or virtually not dissolved under the quench conditions in the quench NMP solvent, and are removed from the quench apparatus in predominantly gaseous form.

25 The lower the quench temperature, the higher the proportion of water and secondary components which have a lower boiling point than PN (at the same pressure) (for example benzonitrile, tolunitrile) in the liquid quench effluent.

30 In a particular embodiment of the process according to the invention, before the hydrogenation of the phthalonitrile, water and any products having a boiling point lower than phthalonitrile (at the same pressure) (low boilers; for example, unconverted xylene, benzonitrile, tolunitrile, each as a heteroazeotrope with water, water, benzonitrile, tolunitrile; listing with increasing boiling point (at the same pressure); and in some cases also o-, m- or p-methylbenzylamine, benzylamine, xylylenediamine, 35 these amines stemming from recycled solvent from the hydrogenation stage) may therefore be partly or fully removed by distillation from the resulting quench solution or suspension.

This removal of the low boilers is effected preferably in a distillation column via the top.

Preference is given to using a distillation column which is equipped preferably with the customary internals for increasing the separating performance, such as trays, structured or random packings, etc.

5 The configuration of the column (in particular number of separating stages, feed point, reflux ratio, etc.) may, adapted to the particular composition of the solution or suspension, be carried out by those skilled in the art by methods familiar to them. Preference is given to operating under reduced pressure, in order to limit the bottom temperature.

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Hydrogenation:

The resulting quench solution or suspension is subsequently fed to the hydrogenation. Optionally, further NMP or a further organic solvent, for example xylene, benzylamine,

15 o-, m- or p-methylbenzylamine, xylylenediamine and mixtures thereof may be added beforehand to the quench solution or suspension.

It is thus a characterizing feature of the process according to the invention that the phthalonitrile obtained as an intermediate is not isolated in substance. The

20 phthalonitrile to be hydrogenated is not removed from the NMP used in the quench step for the hydrogenation stage.

In the process according to the invention, there is preferably no removal of high boilers, i.e. of products having a boiling point higher than phthalonitrile (at the same pressure)

25 from the quench solution or suspension.

For the hydrogenation of the phthalonitrile to the corresponding xylylenediamine (o-, m- or p-xylylenediamine), particular preference is given to adding ammonia, preferably in liquid form, to the solution or suspension. The ammonia may be added directly after the

30 quench stage or not until the hydrogenation stage

The weight ratio in the fresh feed of dinitrile to ammonia here is generally from 1 : 0.15 to 1 : 15, preferably from 1 : 0.5 to 1 : 10, more preferably from 1 : 1 to 1 : 5.

35 For the hydrogenation, the catalysts and reactors (for example fixed bed or suspension method), and also processes (continuous, semicontinuous, batchwise), which are known to those skilled in the art for this reaction may be employed.

In the fixed bed catalyst method, both the liquid phase and the trickle method are

40 possible. Preference is given to a trickle method.

In this regard, reference is made, for example, to the processes described in the applications GB-A-852,972 (equivalent: DE-A-11 19 285) (BASF AG), DE-A-12 59 899 (BASF AG) and to the US patent No. 3,069,469 (California Research Corp.).

5 The hydrogenation reactor may be operated in straight pass. Alternatively, a circulation method is also possible, in which a portion of the reactor effluent is recycled to the reactor inlet, preferably without preceding workup of the circulation stream.

This allows optimum dilution of the reaction solution to be achieved, which has a  
10 favorable effect on the selectivity. In particular, the circulation stream may be cooled in a simple and inexpensive manner by means of an external heat transferor, and the heat of reaction thus removed. The reactor can also be operated adiabatically, in which case the temperature rise of the reaction solution may be limited by the cooled circulation stream. Since the reactor itself then does not have to be cooled, a simple  
15 and inexpensive design is possible. An alternative is a cooled tube bundle reactor.

Preference is given to catalysts which contain cobalt and/or nickel and/or iron, as an unsupported catalyst or on an inert support.

20 The reaction temperatures are generally from 40 to 150°C, preferably from 40 to 120°C.

The pressure is generally from 40 to 300 bar, preferably from 100 to 200 bar.

25 Isolation of the XDA:

After the hydrogenation, the solvent and any ammonia used are distilled off.

Preference is given to purifying the xylylenediamine by distilling off relatively low-boiling  
30 by-products (at the same pressure) via the top and removing relatively high-boiling impurities via the bottom by distillation.

Particular preference is given to the method in which, after the hydrogenation, the NMP, any ammonia and also any relatively low-boiling by-products are distilled off via  
35 the top and, afterwards, relatively high-boiling impurities are removed from the xylylene by distillation via the bottom.

In a particular embodiment, the removal of relatively low-boiling and relatively high-boiling by-products may also be effected in a sidestream or dividing wall column, in  
40 which case pure xylylenediamine may be obtained via a liquid or gaseous sidestream.

Depending on the desired purity, the product (XDA) is additionally extracted with an organic solvent, preferably an aliphatic hydrocarbon, in particular a cycloaliphatic hydrocarbon, very particularly cyclohexane or methylcyclohexane.

5 This purification by extraction may be effected, for example, according to DE-A-1 074 592.

A schematic overview of a preferred embodiment of the process according to the invention is given by figure 1 in the appendix.

10 The optional process steps, 'water removal' and 'extractive XDA purification' are indicated by dashed lines.

#### Examples

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##### Example 1:

20 Ammonoxidation of m-xylene, subsequent quenching of the reaction gases with NMP as a solvent and hydrogenation of the IPN formed in the ammonoxidation stage (cf. process scheme in figure 1)

25 A catalyst having the composition  $V_4Sb_3W_{0.4}Cs_{0.2}$  on steatite was installed into a tubular reactor as a fixed bed. The apparatus was heated externally to 400°C. Evaporated m-xylene, gaseous ammonia, air and nitrogen were introduced to the reactor ( $NH_3$  / m-xylene = 8 mol / 1 mol;  $O_2$  / m-xylene = 4 mol / 1 mol). The furthest upstream part of the reactor was filled with an inert bed, so that the starting materials reached the reaction zone premixed and preheated to 400°C. In the reactor there was a slightly elevated pressure of from 0.02 to 0.03 bar. The hotspot temperature reached 450°C. After conversion (C) of m-xylene of 79%, a selectivity (S) for IPN of 68% was achieved.

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The gas mixture leaving the reactor is quenched in a column with NMP. A solution of IPN in NMP is discharged from the quench column at 122°C and contains 0.6% by weight of m-xylene, 1.6% by weight of water, 0.1% by weight of benzonitrile, 4% by weight of tolunitrile, 27% by weight of IPN and approx. 66.7% by weight of NMP.

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Unconverted reaction gases and inert gases, and also unconverted m-xylene and a little NMP, are withdrawn in gaseous form via the top of the quench column. This gas may be worked up, in order to recycle the materials of value (in particular  $NH_3$ , m-xylene, NMP and tolunitrile) into the reaction stage or into the quench circuit. Inerts and secondary components ( $H_2O$ , benzonitrile,  $N_2$ ,  $CO_2$ , etc.) are discharged from the workup stage.

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A solution corresponding to the calculated composition at the quench outlet, consisting of 0.44 g of m-xylene, 1.7 g of water, 0.88 g of benzonitrile, 3.1 g of tolunitrile, 24 g of IPN and 58 g of NMP, was mixed together from the pure components and fed to the hydrogenation. For the hydrogenation, liquid NH<sub>3</sub> was metered into the mixture

5 (NH<sub>3</sub>/IPN = 14 mol/1 mol). The hydrogenation was effected in the presence of H<sub>2</sub> and 5 g of Raney nickel catalyst at 100°C and a pressure of 100 bar in a stirred autoclave. The conversion of IPN was quantitative, and a yield of 92% based on IPN used was obtained.

10 (The data of the quench step reported above are the results of a thermodynamic simulation. In this simulation, the quench was considered to be an apparatus in which there is thermodynamic equilibrium between gas and liquid phase. In addition to the pure material data of the components involved, real binary data were used in the calculation. Such calculations can be carried out with commercial calculation programs,

15 here: Aspen Plus, which are familiar to those skilled in the art.)

Example 2:

The ammonoxidation was carried out as in example 1, except that the exit temperature from the quench was 91°C. The water content of the solution was 5.2% by weight. The solution is fed to a column having 15 bubble-cap trays. The feed is to the 6th bubble-cap tray. The water is removed together with other components (dissolved gases, m-xylene, benzonitrile, tolunitrile, the latter as an azeotrope with water) via the top. A virtually anhydrous solution consisting of approx. 27% by weight of IPN, 67% by weight of NMP, 6% by weight of tolunitrile and 600 ppm by weight of benzonitrile is obtained via the bottom.

A mixture consisting of 27% by weight of IPN and 73% by weight of NMP, which was mixed together from the pure components, was hydrogenated in a continuous 70 ml tubular reactor over an unsupported cobalt catalyst at 80°C and 190 bar. Every hour, 70 g of IPN solution and 90 g of ammonia were passed over the catalyst. The yield of MXDA was 96% based on IPN used.

(The data of the quench step reported above are the results of a thermodynamic simulation carried out as in example 1).

Example 3:

A mixture consisting of 27% by weight of IPN and 73% by weight of NMP, which was mixed together from the pure components, was hydrogenated in a continuous 70 ml tubular reactor over an unsupported cobalt catalyst at 80°C and 190 bar. Every hour, 70 g of IPN solution and 54 g of ammonia were passed over the catalyst. The same

volume flow rate was recycled as a solvent. The yield of MXDA was 95.5% based on IPN used.

Example 4:

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A mixture consisting of 15% by weight of IPN and 85% by weight of NMP which was mixed together from the pure components was hydrogenated over an unsupported cobalt catalyst at 80°C and 190 bar in a continuous 70 ml stirred reactor. Every hour, 140 g of IPN solution and 72 g of ammonia were passed over the catalyst. The yield of

10 MXDA was 96% based on IPN used.

Example 5:

Ammonoxidation of m-xylene, subsequent quenching of the reaction gases with NMP as

15 a solvent

A catalyst of the composition  $V_4Sb_3K_{0.4}Ba_{0.2}$  on steatite was installed into a tubular reactor at a fixed bed. The apparatus was heated externally to 415°C. Evaporated m-xylene, gaseous ammonia and air were fed to the reactor ( $NH_3$  / m-xylene = 14 mol / 20 1 mol;  $O_2$  / m-xylene = 4 mol / 1 mol). The catalyst of the first half of the reactor was diluted with 70% by weight of steatite spheres, the second half with 40% by weight. In the reactor, there was a slightly elevated pressure of 0.02 bar. The hot spot temperature reached 430°C. At a conversion of m-xylene of 88%, a selectivity for IPN of 71% was obtained.

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The gas mixture leaving the reactor is quenched with NMP in a column. A solution of IPN in NMP is discharged from the quench column at 120°C and 1.02 bar (abs.) and contains 0.25% by weight of m-xylene, 1.3% by weight of water, 3.6% by weight of tolunitrile, 27% by weight of IPN and approx. 67.7% by weight of NMP. Unconverted 30 reaction gases and inert gases and also unconverted m-xylene and a little NMP are removed in gaseous form via the top of the quench column. This gas may be worked up in order to recycle the substances of value (in particular  $NH_3$ , m-xylene, NMP and tolunitrile) into the reaction stage or into the quench circuit. Inerts and accompanying components ( $H_2O$ ,  $N_2$ ,  $CO_2$ , etc.) are discharged from the workup stage.

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(The data of the quench step reported above are the results of a thermodynamic simulation, carried out as in example 1).

Example 6:

Investigations of solubility of IPN in different solvents

5 The solubility of IPN in NMP is approx. 26% by weight at 60°C and approx. 41% by weight at 90°C.

At 90°C, pseudocumene attains a solubility of only 20% by weight and mesitylene of only 12% by weight.

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At 60°C, the solubility of IPN in mesitylene or pseudocumene is in each case below 10% by weight.